

CHARACTERIZATION OF CHARS FROM PYROLYSIS OF CHLOROGENIC ACID

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INTRODUCTION

Chlorogenic acid is a plant material that contains both phenolic and saccharide groups and can be a good representative model compound for biomass. It is one of the components of coffee seeds and tobacco leaves. Commercially, chlorogenic acid is extracted from coffee seeds. When pyrolyzed, chlorogenic acid is reported to undergo a rapid decomposition to form a gaseous product and a solid char. The char then undergoes further reactions to form additional product [1]. A number of studies are reported in the literature on the composition of the gaseous product from chlorogenic acid. Zane and Wender [2] heated a sample of chlorogenic acid in a flask at 600°C for 5 min and observed catechol, 4-methyl catechol, 4-ethyl catechol, benzoic acid, and quinine as the main components. Sakuma *et al.* [1] reported, in addition, phenol and 4-vinyl catechol. Schlottzauer *et al.* [3] pyrolyzed chlorogenic acid at 800°C and observed 5-hydroxymethyl furfural in addition to the above products. These studies indicate that the composition of the gaseous product is dependent on the pyrolysis conditions. Although considerable work has been done on the analysis of the gaseous product, there is no information in the literature on the nature and composition of the product char or the effect of pyrolysis conditions on char characteristics. The nature of the char may govern the extent of secondary reactions.

In this work, the effect of pyrolysis conditions on the yield and nature of chars from chlorogenic acid was studied. The chars were produced at atmospheric pressure under oxidative and non-oxidative (inert) atmospheres and at temperatures ranging from 250° to 750°C. The non-oxidative runs were made with helium as the carrier gas; the oxidative runs with a mixture of 2% oxygen in helium. The concentration of oxygen in the oxidative runs was kept low to prevent a complete combustion of the substrate. The uncondensed gaseous product was analyzed by mass spectrometry. The product char was characterized in terms of its elemental analysis and surface area and by solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy and Fourier-transform infrared (FTIR) spectroscopy. The surface morphology of char was studied by scanning electron microscopy (SEM). The results of char characterization are discussed in relation to the evolved gases.

EXPERIMENTAL

Chlorogenic acid was obtained from Fisher Scientific. It is predominantly the *trans* isomer with 99% purity. The pyrolysis reactor was a 1/2" diameter quartz tube heated by a 6" long metal-block furnace. The furnace provided about 4" length of uniform temperature profile. The runs were made at atmospheric pressure and temperatures ranging from 250° to 750°C. Up to 300 mg of chlorogenic acid was pyrolyzed in each run which lasted 10 min. The carrier gas was passed continuously over the sample at a flow rate of 220 ml/min. A sample of the uncondensed gaseous product was analyzed on-line by a Balzer QMG511 quadrupole mass spectrometer.

The elemental analysis of the product char was performed at Galbraith Laboratories, Inc. The BET surface area was measured in automated volumetric gas adsorption apparatus (Autosorb 1 from Quantachrome Co.) using nitrogen as an adsorbate. The ¹³C CPMAS NMR spectra were obtained on a Varian Unity 200 spectrometer at a carbon resonance frequency of 50.3 MHz. The MAS spinning speed was ~8100 Hz. The infrared spectra were recorded on a Spectra-Tech IR-Plan microscope interfaced to a Nicolet Magna 560 FTIR spectrometer. The sample was mounted between two KBr plates held in a micro-compression cell. For the SEM analysis, a Topcon SM720 Field Emission Scanning Electron Microscope was used.

RESULTS AND DISCUSSION

Char Yield

Figure 1 shows the effect of temperature on the yield of the solid product, *i.e.* char yield, from chlorogenic acid. In non-oxidative runs, the yield decreases with increase in temperature from 80% at 250°C to 20% above 600°C. The oxidative runs (with 2% oxygen in helium) result in char yields which, at low temperatures, are virtually identical to those from the non-oxidative pyrolysis but are lower (than in non-oxidative runs) at high temperatures. Above 550°C, virtually all the char was converted to gaseous product in the oxidative runs. Interestingly, the char yields are not dependent on the mass of chlorogenic acid pyrolyzed. This indicates that the pyrolysis reactions may not be transport-limited under the pyrolysis conditions used in this study. A preliminary analysis of the data indicated activation energy of 40 kJ/mol for the non-oxidative pyrolysis and 300 kJ/mol for the oxidative pyrolysis. The activation energy for non-oxidative

pyrolysis is rather low. On the other hand, the activation energy for oxidative pyrolysis is typical of that associated with the char oxidation. The gaseous product consisted mainly of phenol, catechol, benzene, and benzoic acid in addition to water, CO and CO₂. Similar products are reported in the literature [2,3]. Above 600°C, in this study, the gaseous product also contained significant hydrogen.

Char Characterization

The product char was obtained as a volcano-like cone having a smooth and 'glassy' external surface. This indicates that the chlorogenic acid forms a melt at relatively low temperature, which is consistent with its melting point (208°C). SEM analysis of chars indicated that the decomposition of chlorogenic acid was accompanied by the formation of bubbles in the melt. The bubbles grew as the reaction proceeded until they broke allowing the gaseous products to escape. The formation, growth, and breaking of bubbles and, in turn, the evolution of the gaseous product and char, were controlled by the pyrolysis conditions. At low temperatures, the char particles were of irregular appearance with a few bubbles inside. At higher temperatures, the particles became more rounded and the bubbles grew larger and, in some cases, the bubble film was broken probably by the escaping gases which may have been released into another closed bubble or to outside. The surface of the melt became increasingly rough due to the growth of globular, rod-like, and platelet structures which decomposed further to leave a carbonized frame of bubbles and pores. Figure 2 shows a typical SEM micrograph of the surface of the char at 650°C. Some of the bubbles are seen to be intact. The char is almost completely carbonized at this temperature. In the presence of oxygen, these carbonized structures were oxidized completely above 550°C.

The hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios for the chars at different temperatures are plotted in Figure 3. Both the ratios decrease sharply with increase in the pyrolysis temperature indicating that the char becomes increasingly more carbonaceous in nature at high temperatures. Further, the H/C ratio decreases almost linearly with the decrease in the O/C ratio until about 650°C. The major reactions at these temperatures appear to be the dehydration and decarboxylation reactions. However, above 650°C, the H/C ratio drops dramatically relative to O/C ratio indicating a direct dehydrogenation of the product char. This is consistent with the analysis of the gaseous product. Interestingly, the use of oxidative atmosphere does not alter the H/C and O/C ratios significantly relative to those in the non-oxidative case at the same temperature. This may be due to the low concentration of oxygen in the carrier gas.

The BET surface area measurements indicated that the chars prepared below 550°C had a negligible surface area but that the area increased dramatically to 196 m²/g at 650°C, before decreasing slightly at 750°C. Thus, the use of high temperatures seems beneficial in creating a char with a high surface area. The presence of oxygen also enhanced the surface area to a maximum of 90 m²/g at 450°C. Thus, the presence of oxygen appears to affect the physical characteristics of char.

The solid-state ¹³C CP/MAS NMR spectra of chars are presented in Figure 4. The multiplicities of resonances in the individual groups of peak are due to multiple crystalline modifications and/or multiple molecules in the crystalline lattice. The spectrum for chlorogenic acid (not shown) indicated that the chlorogenic acid is mainly crystalline in nature and contains aliphatic, aromatic, phenolic, carbonyl, and carboxyl structures. The spectra of chars (Figure 4) differ progressively with temperature from that of the chlorogenic acid. At 250°C, the resonance bands tend to be broad indicating an increase in the amorphous nature of the sample compared to chlorogenic acid. Since the resonance bands do not change appreciably in number or intensity, the changes appear to be mostly due to melting and the formation of an amorphous state. Above 250°C, there is a steady loss of oxygen functionality indicated by the loss of carbonyl absorptions. The spectrum for the 350°C char shows that the phenolic, carboxyl and carbonyl groups are still present, although the concentration of the latter two groups is considerably small. It is believed that the aliphatic and oxygen groups create links and loops between aromatic clusters of various sizes [4]. As the temperature is increased further, the char loses its aliphatic character completely and becomes more and more aromatic in nature. The resonance bands corresponding to carbonyl groups disappear mostly. The resonances corresponding to phenolic groups also decrease progressively in intensity until they become almost totally absent in the 650°C char. The oxygen-bonded carbons are no longer distinguishable and only a very small aliphatic peak remains, indicating a complete carbonization of the char. The char at 750°C could not be analyzed due to its high conductivity. Essentially similar observations were made from the NMR analysis of the oxidative chars, suggesting that many of the carbons in the chars that react with oxygen were lost probably by oxidation. These results appear to be at variance from those for chars prepared from cellulose [5] where it was observed that the aliphatic resonance of the char was significantly reduced while the resonance of aromatic carbons bonded to oxygen

increased. The difference could be due to differences in substrates as well as in pyrolysis conditions.

The FTIR results, presented in Figure 5, also suggest large chemical changes in chlorogenic acid above 250°C. Both the hydroxyl and carbonyl groups are gradually lost as the pyrolysis temperature is increased although the loss in hydroxyl groups does not appear to be as rapid as that in the carbonyl groups. The aliphatic character of char also decreases at high temperatures. On the other hand, the aromatic character, the C=C and the aromatic ring activities increase and are highest at 650°C. At 750°C, all the bands due to OH, CH, CH₂, and CH₃ stretches have vanished and there is a weak band for C=O. The char is mainly an aromatic polymer of carbon atoms. The spectra show an increasingly large drift in the baseline at high temperatures, which could be due to increase in the carbon black-content of the char as a result of increased carbonization. Boon *et al.* [6] observed a similar loss of oxygen functionality and an increase in the aromatic character with the cellulose chars at high temperatures. As in NMR analysis, the FTIR analysis showed essentially no effect of oxygen on the char characteristics.

The results of characterization are consistent with the evolution of the gaseous products. As the pyrolysis temperature is increased, the char loses most of its oxygen and hydrogen to the gaseous products such as water, CO, and CO₂, and becomes more carbonaceous in nature and low in crystallinity. The char probably also undergoes a direct dehydrogenation at high temperatures.

CONCLUSIONS

The char yield from chlorogenic acid was enhanced by low heating rates and low temperatures but was independent of the mass of substrate pyrolyzed, at least up to 300 mg. The major components of the gaseous product were catechol, phenol and benzoic acid. The surface area of char increased with temperature to a maximum at 650°C. The oxidative pyrolysis enhanced the surface area but decreased the char yield. The char lost its carbonyl, carboxyl, and aliphatic functionalities completely above 550°C. As a result, the carbonaceous and aromatic character of char increased with temperature and was highest at 750°C.

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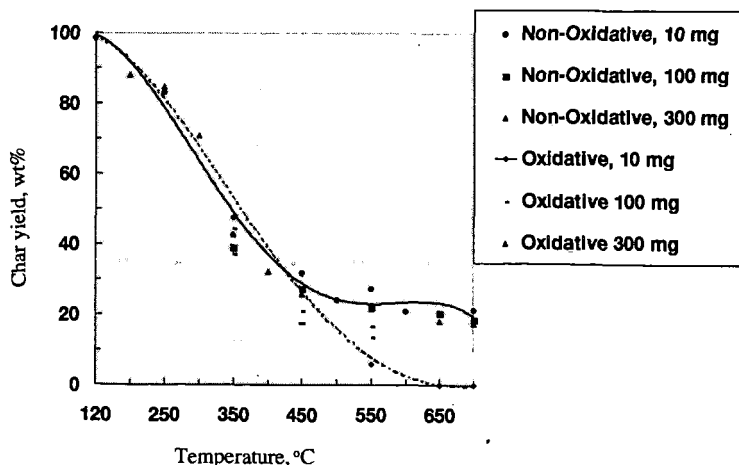


Fig. 1- Effect of temperature on char yield from chlorogenic acid

Char / SEM

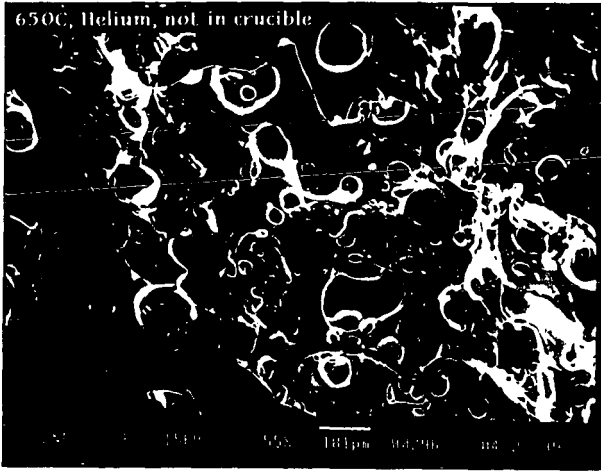


Fig. 2- Surface morphology of the 650°C-char.

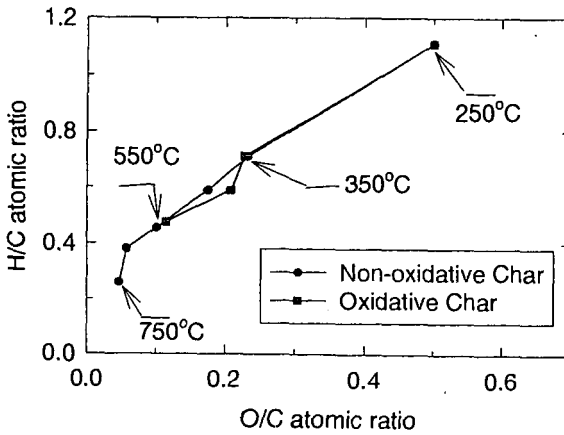


Fig. 3- Relationship between H/C and O/C ratios of chlorogenic acid chars

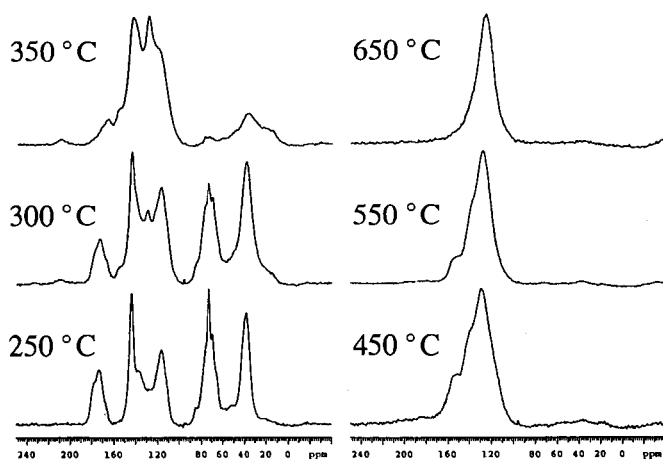


Fig. 4- Solid-state ^{13}C CPMAS NMR spectra of chlorogenic acid chars

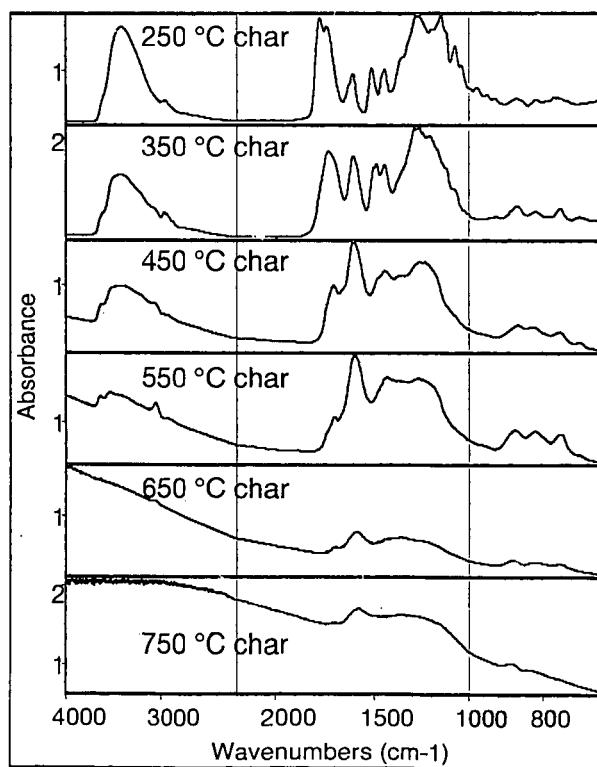


Fig. 5- Fourier-transform infrared (FTIR) spectra of chlorogenic acid chars